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AGEING EFFECTS IN THIN ANODIC OXIDE FILMS  
ON Au IN  $\text{HClO}_4$

by  
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In a previous paper<sup>(1)</sup> it was shown that the properties of thin oxide films on Au depend strongly on the potential,  $E_a$ , at which they are formed. Thus, as the potential is increased the amount of oxide on the electrode increases, being a monolayer at about 1.45v vs.  $H_2/H^+$  in the same solution. In addition, the reduction of a potentiostatically preformed oxide becomes more difficult at higher potentials of formation, although the reduction is still quantitative<sup>(2)</sup>. In this paper, some experiments are reported which indicate that the properties of the anodically formed films are sensitive also to the time for which they are formed,  $\tau_a$ . In effect, the oxide is growing slowly even at long times of formation and becomes harder to reduce. Ageing effects of this kind are well known for thick oxide films<sup>(3)</sup>, but very little is known about the ageing of very thin films. Frumkin<sup>(4)</sup> reports such effects for anodically formed films on Pt; however, there appears to have been no quantitative investigation of this phenomenon.

#### EXPERIMENTAL PROCEDURE

Oxides were formed at each potential by means of a Wenking fast rise potentiostat. To measure the extent of oxidation,  $Q_a$ , the oxides were usually reduced galvanostatically at  $\sim 300 \mu a/cm^2$ . Switching of the counterelectrode from the potentiostatic to the galvanostatic circuit was achieved with a Hg-wetted relay. The potential-time transient was followed on an oscilloscope via a high impedance voltage follower (Philbrick P2 amplifier used as electrometer). The method of determining from the oscilloscope traces the amount of oxide and the potential of reduction of the oxide has been described previously<sup>(1)</sup>. Usually, a large part of the oxide is reduced at a constant potential. However, at short times of formation and/or at low potentials of formation and/or with large reduction currents, the oxide reduction curve (chronopotentiogram) shows a sloping portion rather than a flat plateau. In these cases, the first potential at which the oxide starts to be reduced was used in assessing the reduction potential of the oxide at the given current density. This is illustrated in

Fig. 1. For reduction experiments with linear potential sweeps, an Exact Electronics function generator (Model 250) was used to generate the potential ramp, and the potential across a decade resistance box (General Radio Company, 0.05%) was recorded with an oscilloscope. In some cases, two plug-in units were used in the oscilloscope, allowing an X-Y presentation.

In other respects, the methods and procedures are as previously described<sup>(1)</sup>. It is to be emphasized that the counterelectrode should also be of Au; if Pt is used, the working electrode is contaminated with what appears to be about a monolayer of Pt. Experiments were carried out in 1N HClO<sub>4</sub> at room temperature (23° ± 2°C). A hydrogen reference electrode was used, and potentials are reported against Pt, H<sub>2</sub>/H<sup>+</sup> in the test solution.

## RESULTS AND DISCUSSION

Growth of the Oxide – Fig. 2 shows some results during the latter stages of the oxide growth for the extent of the electrode oxidation as a function of time at each potential. Growth of the oxide appears to follow a semi-logarithmic relationship, i.e.,

$$Q_a = a + b \log \tau_a \quad (1)$$

where  $a$  and  $b$  are constants. At the shortest anodization times used here, 2 sec, most of the oxide has already formed. Thus, at 1.85v, the oxide is already at 82% of its 5-min value after 2 sec of formation and, at 1.45v, it is 88% of its 5-min value. However, it appears from information available in the literature for the growth of thin oxide films on Pt (5, 6), particularly from the data of Gilman<sup>(6)</sup>, we may have considerable confidence in the applicability of Eq. (1) to the earlier stages of the oxide growth. If these oxides are considered as adsorbed layers rather than as distinct compounds<sup>(7)</sup>, then Eq. (1) would follow from the application of the Temkin adsorption isotherm, sometimes known as Elovich kinetics<sup>(8)</sup>. We may estimate a monolayer of oxide as 400<sup>(1)</sup> or 450<sup>(9)</sup>, or 650<sup>(9)</sup>  $\mu\text{coul}/\text{cm}^2$ , but whichever of these is the most reasonable, the present data extend from less than a

monolayer to considerably above a monolayer. Despite this, there is a smooth variation of the parameter  $b$  of Eq. (1) with  $E_a$  (Fig. 3).

As expected, the growth rate of the oxide is higher, in absolute terms, at the higher potentials of formation, and also, as indicated above, the fractional growth (2 sec to 5 min) is more at the higher potentials. Although the growth rate is relatively slow even at the highest potentials (Fig. 2), the equating previously<sup>(1)</sup> of the 5-min value of  $Q_a$  with its infinite time value does involve small errors in the  $Q_a$  values presented, as does the procedure used by Laitinen and Chao<sup>(10)</sup>. For example, at 1.85v the 5-min values should perhaps be about 8% less than the 1-hr value of  $Q_a$ . However, it is unlikely that the oxide thickens indefinitely, for as has been observed at the higher potentials<sup>(1,2)</sup>, the oxide has a finite rate of dissolution; hence the error in selecting the 5-min values of  $Q_a$  would be less than this. In fact very little difference was found between the 5-min and 20-min values of  $Q_a$ <sup>(1)</sup>.

Reduction of the Oxide – The reduction kinetics of the oxide are shown in Fig. 4 as a function of  $E_a$  and  $\tau_a$ . It is seen that at a given potential of formation the oxide becomes progressively harder to reduce with longer times of formation. At any potential of formation, the general effect is a shift of the Tafel line for the reduction of the oxide (slope 39-41 mv) to lower potentials. At the shorter times of formation, however, the slope tends to be less than the usual value, particularly at the lower potentials. As has been noted, reduction potentials in this region are the least reliable as the chronopotentiogram has the least satisfactory plateau.

The time variation of the oxide reduction kinetics is more pronounced at the lower potentials of formation. The oxides stabilize much more rapidly at their ultimate (5 or 10 min) properties at higher potentials of formation; this is despite the fact that the oxide, at the higher potentials, is much "thicker" (if "thickness" is the relevant term for  $\sim 0.8 \leq$  layer thickness  $\leq 2$  layers) and, thus, presumably, any transport processes through the film would be more difficult. On the other hand, the higher field resulting from the higher potential would help to counteract this for ion migration

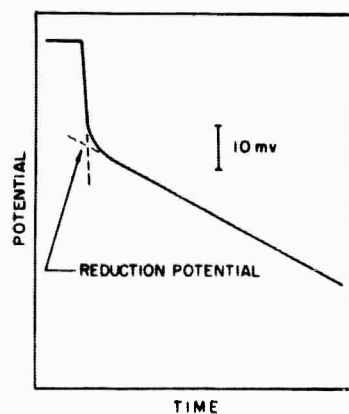


Fig. 1. Estimation of the reduction potential from chronopotentiograms when the oxide reduction takes place over a range of potentials.

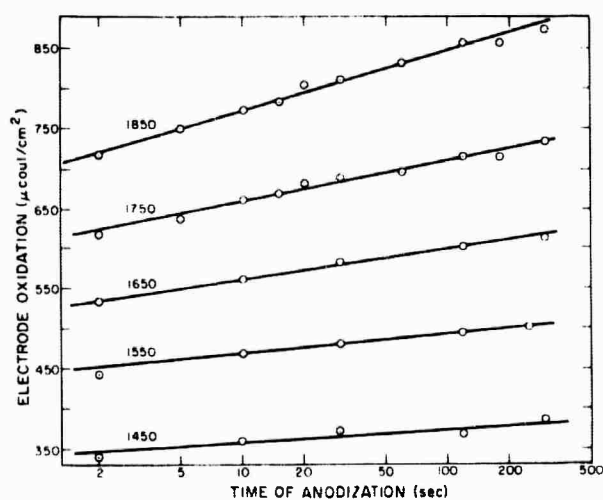


Fig. 2. Growth of oxide at various potentials (mv vs. R.H.E.) as a function of time.

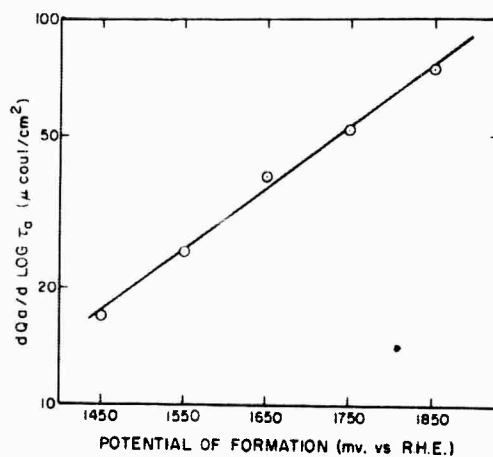


Fig. 3. Semi-logarithmic expression of the growth-rate constant  $b$  as a function of potential.

processes through the film. So, although there is both relatively and absolutely a much larger change in the quantity of oxide formed during the range of  $\tau_a$ , 2 sec to 5 min, at the higher potentials of formation, the properties of the oxide change much more, during this time, at the lower potentials of formation.

Use of Triangular Potential Sweeps for Oxide Reduction – It is clear from the data presented here that triangular sweeps are to be employed for studies of oxide reduction only with extreme caution. In the method of Will and Knorr<sup>(11)</sup>, the oxide is formed over a range of potentials, and not only is this likely to lead to an inhomogeneous oxide per se<sup>(1)</sup>, but also the oxide has only a fraction of a second to "age". Consequently, we would not expect the results obtained on the cathodic sweep of the triangles to be quantitatively significant. This is apparent from the curves shown in Fig. 5. These represent the current potential curves for the reduction of oxide formed under various conditions. Curve A is the current-potential curve for the reduction of oxide formed for 5 min (i. e.,  $\approx$  infinite time) at 1500 mv. A full description of such curves will be given later. Curves B and C represent the reduction of oxide formed during the anodic part of a 0.14 v/sec triangular wave. In B, the triangle was terminated at 1500 mv, in C at  $\sim$  1600 mv. As expected, A and B are not comparable, relatively little oxide being formed in B. C was chosen such that  $Q_A = Q_C$ . We note that the oxide in C is more easily reduced and, also, is reduced over a wider range of potential (i. e., the peak is shorter and squatter). A comparison of B and C indicates that a considerable part of  $Q_C$  is formed between 1500 and 1600 mv, i. e., at a higher potential than the top potential of A. From the previous work<sup>(1)</sup> it would, therefore, be supposed that the oxide in C would be harder to reduce than that in A. Thus, the main reason why curve C indicates an oxide which is misleadingly easy to reduce is because the oxide has not had enough time to "age". The broadness of the peak in C would indicate that the oxide is unusually inhomogeneous compared with A. The reduction curves obtained after various times of formation at a fixed potential (Fig. 6) do not indicate that unaged oxide is usually more inhomogeneous than the aged material; for example, the width of the reduction

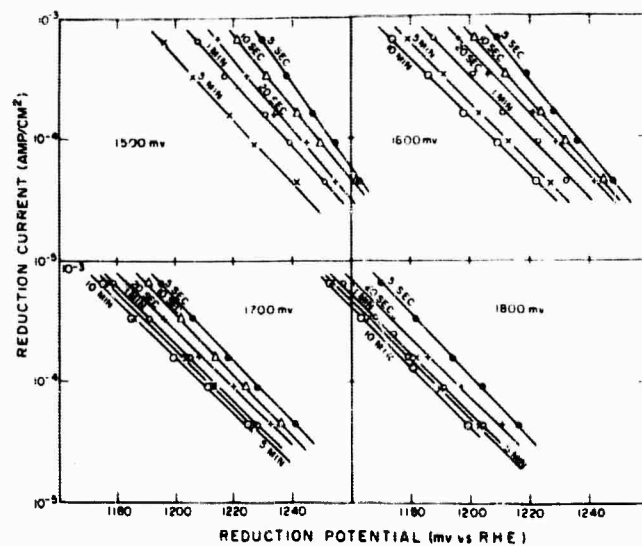


Fig. 4. Current-potential curves for the reduction of oxides, as a function of time and potential of formation.

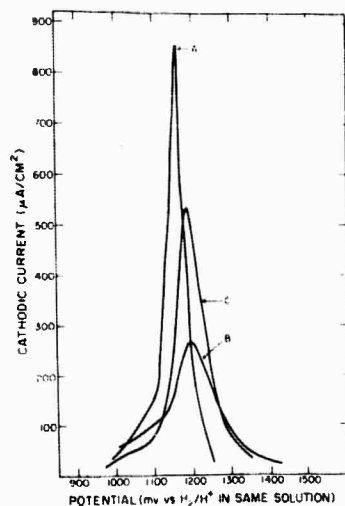


Fig. 5. Current-potential curves for the reduction of oxides, made with linear potential sweeps of 0.14 v/sec. Curve A, oxide reduced after 5 min at 1500 mv; curve B, oxide formed and reduced during triangular potential sweep, reversed at 1500 mv; curve C, triangular sweep reversed at ~ 1600 mv, such that  $Q_A \approx Q_C$ .

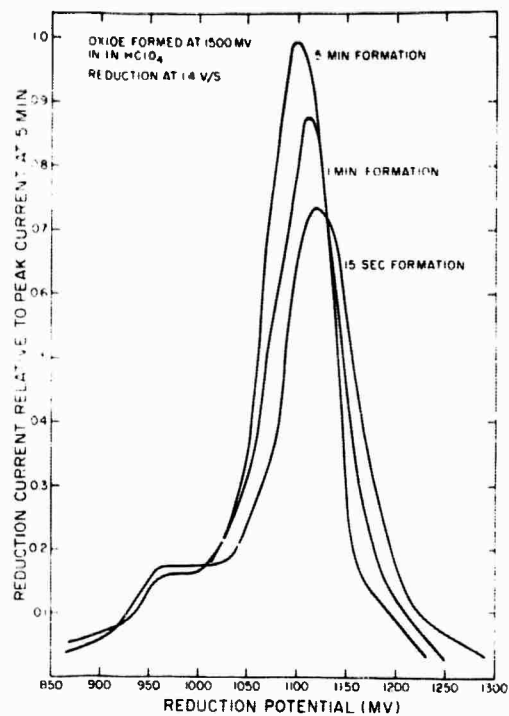


Fig. 6. Current-potential curves for the reduction of oxides, made with linear potential sweeps of 1.4 v/sec, as a function of time of formation at 1500 mv.



peak at the current corresponding to half the maximum current is the same for each time of formation, about 80 mv in this instance. Thus, the inhomogeneity of the oxide in C, which is too large to be associated solely with the formation of oxide over a range of potential per se<sup>(1)</sup>, must result mainly from the "freezing-in" of oxide configurations formed at short times at the lower potentials. These configurations will not have "aged" out in the short time before the cathodic sweep. In order to avoid such errors, say to keep the reduction potential at a given current to less than 5 mv with respect to the 5 min values, we would have to allow at least 2 min at 1600 (cf. Fig. 4). This involves extremely slow sweep rates and clearly indicates that the method of Will and Knorr<sup>(11)</sup> is not suitable to study such reactions quantitatively.

### SUMMARY

1. The properties of anodic oxide films on Au in 1N HClO<sub>4</sub> have been studied as a function of time (2 sec to 5 min) and of potential of formation (1450 to 1850 mv vs. Pt, H<sub>2</sub>/H<sup>+</sup> in the same solution).
2. Over the range observed (10-20% of the total oxide), the oxide grows slowly with time, apparently according to Elovich kinetics, although the constants are potential-dependent.
3. Oxides formed at longer times at a given potential are harder to reduce.
4. This "ageing" effect is greatest at the lower potentials of formation, despite the greater thickness of the oxide at the higher potentials and despite the larger change in the amount of oxide at the higher potentials.
5. Because of these ageing effects, the triangular sweep method of Will and Knorr is not suitable to study these films.

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